DIELECTRIC ABSORPTION OF 3.14 CM MICROWAVES IN SOME POLAR LIQUIDS—PART II. SUBSTITUTED HALO-BENZENES AND NAPHTHALENE

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ABSTRACT. The dielectric losses of chloro-, bromo-, metadichloro- and 1, 2, 4-tri-chlorobenzene and of α-chloronaphthalene in the liquid state at different temperatures due to absorption of microwaves of wavelength 3.14 cm have been measured and the values of time of relaxation (τ) of all the compounds have been determined. It has been shown from the results that the viscous forces (ζ) inhibiting the rotations of the molecules of these compounds in the liquid state are functions of the macroscopic viscosities (η) of the respective liquids and that the internal friction η_{int} may be put in the form η_{int} = Const. η^{γ}, where γ is the ratio of the molar heats of activation for dielectric relaxation and viscous flow. Further, from a comparison of the τ-values of chloro-, bromo- and metadichloro- benzene and of α-chloronaphthalene in the liquid state with the τ-values of the respective compounds in solution in non-polar solvents with viscosities equal to or greater than that of the respective pure liquids, it has been concluded that at least in the present case of liquids having molecules with dipole moment about 1.5 D, the dipolar interactions have only minor effect on the times of relaxation of the molecules.

INTRODUCTION

The time of relaxation of some organic polar molecules with rigid dipoles such as chlorobenzene, bromobenzene, α-chloronaphthalene etc. in the liquid state and in dilute solution in benzene at different temperature in different radio frequency regions were investigated by many workers (Whiffen and Thompson, 1946, Hennelly *et al.*, 1948, Fischer, 1949, Curtiss *et al.*, 1952, William 1959, Smyth 1955). Smyth (1955) made a comparison of the τ-values of a number of organic molecules in the liquid state and in solutions in benzene at a certain temperature and concluded that the larger values of τ in the pure liquid compared to those in dilute solutions might be due to dipolar interactions in the liquids which are almost absent in very dilute solutions. In making such conclusion the effect of the difference in the viscosities of the two media on τ-values has not been properly taken into account. The object of this investigation was to study how the dipole-dipole interactions influence the τ-values of molecules with rigid dipoles in the liquid state and as such a systematic investigation on the τ-values of some molecules with rigid dipoles in the liquid state and in solution in non-polar solvents at

different temperatures was undertaken so that the effect of the viscosity, temperature and other parameters could be considered. The results are also expected to throw some light on the dependence of the internal friction on macroscopic viscosity of the medium.

In a previous communication (Bhattacharyya *et al.* 1964) it was shown that in the case of some polar alkyl benzenes in the liquid state composed of molecules with dipole moments about 0.5D, such dipolar interactions are negligible. In the present paper the results of investigation on some substituted benzenes and naphthalene with rigid dipoles having dipole moments about 1.5D have been discussed

EXPERIMENTAL

The compounds studied in the present investigation are chlorobenzene, bromobenzene α-chloronaphthalene, metadichloro-benzene and 1, 2, 4-trichloro benzene All the chemicals, obtained from reputed firms, were of chemically pure quality. These were first fractionated and the proper fractions were repeatedly distilled under reduced pressure and dried by usual methods before being used in the investigation The experimental arrangement for the determination of dielectric loss at 3 cm is as shown in Figure I.

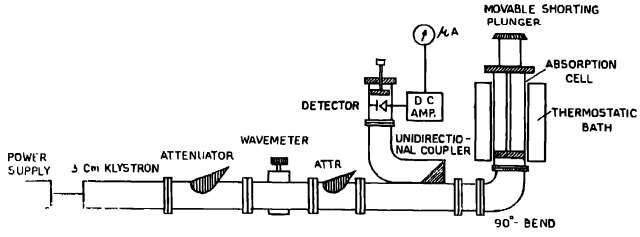

Fig 1 Schematic diagram of experimental arrangement for determining dielectric loss at 3.14 cm.

ϵ' and ϵ'' were calculated from the variations of the reflected power as the shorting plunger is moved in the liquid filled wave guide absorption cell. The magnitudes of the maximum and minimum power and the distance between the successive minima were used for the calculations of ϵ' and ϵ'' following the method due to Surber (1948) The temperature of the absorption cell was maintained constant with the help of a thermostat. The τ-values were calculated from ϵ''-values by using Debye equation for polar liquids as usual. The values of ϵ_0 (static dielectric constant) of all the compounds and the macroscopic viscosities (η) of chloro-bromo- and metadichlorobenzene were taken from standardl literatures. The viscosities of 1 2, 4-trichlorobenzene and α-chloronaphthalene at different temperatures were determined experimentally.

larger because of the presence of dipolar interaction So, it may be inferred that dipole-dipole interactions in these liquids have only minor effect on the τ-values. This conclusion is also expected to hold in the case of α-chloronaphthalene molecules having dipole moments almost the same as those of chloro, bromo- or meta-dichlorobenzene. Moreover, because of greater size of the α-chloronaphthalene molecule and consequently because of greater separation between the dipoles, the dipolar interactions would be less effective than in the above liquids From these consideration it is expected that the τ-values of α-chloronaphthalene in dilute paraffin solution should be greater or at least equal to those in the pure liquid But actually, the reverse is the case. This would suggest that the larger values of τ in the case of α-chloronaphthalene in the liquid state may not be due to dipolar interactions in the liqeid, but may be due to peculiarity in the arrangement of molecules in the liquid state

From these it may be concluded that at least in the case of polar liquids composed of rigid molecular dipoles having moderate moments (about 1 5D), the influence of dipolar interactions on the time of relaxation is less important than that of structural hindrances

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